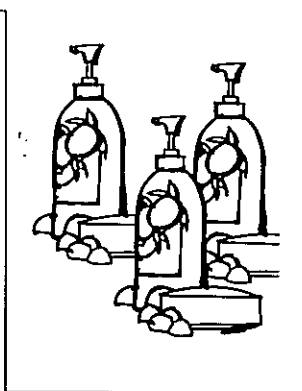# A New Beeswax Derivative for Cosmetic Formulations

By A. W. Peters Rit, Koster Keunen Holland B.V., Bladel, The Netherlands
S. L. Puleo, Koster Keunen Inc., Sayville, New York,
and J. Sprenger, Anschrift der Autoren, Bladel, The Netherlands

Building upon the unique and versatile properties of beeswax, our research has concentrated on creating a product with additional benefits, while retaining as much as possible of the natural wax properties. Such a product has recently been developed, and has been assigned the CTFA name PG-3 beeswax.[*]

After a global overview of existing substitutes and derivatives of natural beeswax, this article will introduce the striking new properties of PG-3 beeswax, which may be used as:
- an emulsion stabilizing consistency regulator,
- an oil gelling agent, and
- a dispersion aid for pigments and other insoluble additives.

Historical Use of Beeswax

Natural beeswax, one of the oldest cosmetic ingredients, is still a key component in many cosmetic products. It is used mostly for its emulsifying and consistency regulating properties. Beeswax is one of the few natural emulsifiers available to the cosmetic chemist. In the well known beeswax/borax system, beeswax furnishes the primary emulsifier (in-situ formation of free wax acid soaps) and also the secondary emulsifier (free wax acids, hydroxyesters, etc.) This creates a complete system without, at least in principle, the need for additional emulsifiers. Another important physical characteristic is the thermoplastic

nature of beeswax, which is utilized in lipstick formulation.

From a dermatological point of view, beeswax is well tolerated by the skin, adds to skin softness and elasticity, and rarely causes sensitivity problems. Not commonly known is that beeswax contains natural antibacterial and germicidal agents as well as natural antioxidants.

The continuing use of beeswax in numerous formulations, performing many different functions, illustrates the versatility of beeswax. Substitutes can at best imitate only some portions of beeswax functions. Furthermore, beeswax fits well into the current trend toward using natural ingredients in cosmetics.

Synthetic Beeswax and Beeswax Substitutes

Considerable effort has been spent on research into beeswax substitutes, but only a few products have reached the market. Most can only mimic some properties of beeswax. For many applications, no satisfactory substitute has been found. Table I summarizes trade names of various synthetic beeswaxes and beeswax substitutes. This list is not complete, but attempts to give a representative choice of available materials.

Reasons given for wanting beeswax substitutes are: less dependence on a single source (the bee), less fluctuation in properties and performance, and possible improvements upon beeswax for certain applications. Hardly any economic reason exists for substituting for beeswax in cosmetics, as price and

[*]Cera Bellina (Koster Keunen)

achieved. A more important reason for substituting beeswax is that, because of its varied and diverse chemical composition, its exact action may vary with source or season. Formulators look for ingredients for which an exact performance can be predicted. Research into substitutes for specific functions of beeswax has resulted in better knowledge of those components which are responsible for the uniqueness of beeswax, and a better understanding of the mechanisms through which these functions are effected.

Beeswax Derivatives

Many natural substances are being used with increasing enthusiasm as cosmetic ingredients. Often they are modified, or a derivative is formed, to improve their performance and to widen their field of application. In this way a whole new range of raw materials with properties desirable for cosmetic use has been created.

Well known examples include lanolin, tallow and coconut oil. However, only a few beeswax derivatives are known. These are of two types: hydrophilic and lipophilic esterification.

In the first type, the wax acids are esterified to hydrophilic groups, thus introducing more surface activity. The resulting waxes are often of the self-emulsifying type.

At the end of the forties, Griffin,[17,18] well known for the first quantitative formulation of the HLB-concept, developed several polyethyleneglycol sorbitol beeswax derivatives (ICI, Atlas G1702-G1734 series), with HLB-values varying from 2 to 9. He also prepared similar lanolin derivatives. Rather high temperatures were used (275°C), reacting beeswax

More than 30 years later Waginaire[19] used a similar process for his product Apifil (Gattefosse) by preparing the polyethyleneglycol derivative of beeswax at a lower temperature (220°C). Improved emulsifying properties are claimed for these products.

In the second type of beeswax derivative, a lipophilic group is esterified to the wax acids. A Japanese patent[20] describes esterification of free wax acids with cetyl, stearyl, and isostearyl alcohols at moderate temperatures (120°C). Some improvements are claimed for formulations using the resulting products in creams and lipsticks.

Not much effort has been put into preparing fractions of beeswax by solvent extraction, vacuum distillation, or crystallization. The prime purpose of separating or concentrating a chemical functionality is to isolate the most active functionality; i.e., to obtain the component(s) thought responsible for the special characteristics of beeswax.[22-24] A recent patent application,[21] uses an extraction technique to separate beeswax into two parts, for one of which improved usage is claimed.

Also worth mentioning in the context of derivatization is the work by Pickthall.[25] Acetylation of the hydroxy functionalities of beeswax showed that these groups play an important part in the emulsifying properties of beeswax.

Product Design

Although PG-3 beeswax is a hydrophilic beeswax derivative, our aim was not just to increase the hydrophilicity of the beeswax. We wanted to create molecules with specific desired properties. From our

Table I. Synthetic beeswax and beeswax substitutes		
Trade Name	Manufacturer	CTFA Adopted Name
B. Wax	International Wax[1-3]	Beeswax
Mismo Beeswax	International wax[1,2]	Beeswax
B. B.	Th. Leonhard[1,2]	Beeswax
Pioneer	Th. Leonhard[1,2]	Beeswax
TL	Th. Leonhard[1,2]	Beeswax
Cutina BW	Henkel[2,4,5]	Glycerylhydroxystearate (and) cetyl palmitate (and) microcrystalline wax (and) trihydroxystearin
Elfacos C26	Akzo[2,6]	Hydroxyoctacosanyl hydroxystearate
Synchrowax BB4	Croda[6]	Synthetic beeswax
Synchrowax BB5	Croda[6]	Synthetic beeswax
Synchrowax BB6	Croda[6]	Synthetic beeswax
Emerwax 1253	Emery (Henkel)[7,8]	Microcrystalline and other waxes
628-5	Frank B. Ross[9]	Paraffin, candelilla, hydrogenated tallow glyceride, stearic acid and cetyl alcohol.
Cerita	M. Argueso & Co.[10]	—
Hydroba-70	Jojoba Growers[11]	—
Iso beeswax	Strahl & Pitsch Inc.[12]	Beeswax, candelilla, soy glyceride, paraffin, carnauba and stearic acid
Lipobee-102	Lipo Chemical Inc.[13]	Synthetic beeswax
Waxenol 821	Caschem[14]	Synthetic beeswax
Vybar 5013	Petrolite[15,6]	Synthetic wax
Cyclochem 326A	Witco[16]	Synthetic beeswax

beeswax are often responsible for granular characteristics: i.e., crystallization behavior and an unsatisfactory gelation of the oil phase.

We therefore decided to eliminate the free wax acids in beeswax by converting them into nonionic amphiphilic molecules with a micelle number larger than 0.6. This micelle value is a numerical relationship of intermolecular functionality, the non-polar carbon chain length to the area of the polar head. The next section will show the importance of molecular design and attractive interaction in micelle formation. Such molecules exhibit bilayered structures as thermodynamically preferred self-assemblies, and show liquid crystalline behavior in a wide concentration range. Nonionic derivatives were chosen because of their compatibility with anionic, cationic and nonionic systems and their low sensitivity to ionic strength.

As important as the type of molecule created is the way in which the reaction is carried out: the choice of the derivative-producing agent, auxiliary agents used, reaction time and temperature, necessary finishing steps, and any other considerations. The resulting modified beeswax yields the analytical values shown in Table II.

Amphiphile Self-assembly Theory

The literature (for example, References 26, 27 and 28) shows that the presence of lamellar liquid crystals leads to increased emulsion and suspension stability. An obvious advantage of lamellar liquid crystals at the emulsion interface is that the responsibility for separating the two phases is now carried by a multilamellar buffer layer, the liquid crystal (LC) third phase, as opposed to a single emulsifier film in a two-phase emulsion system.
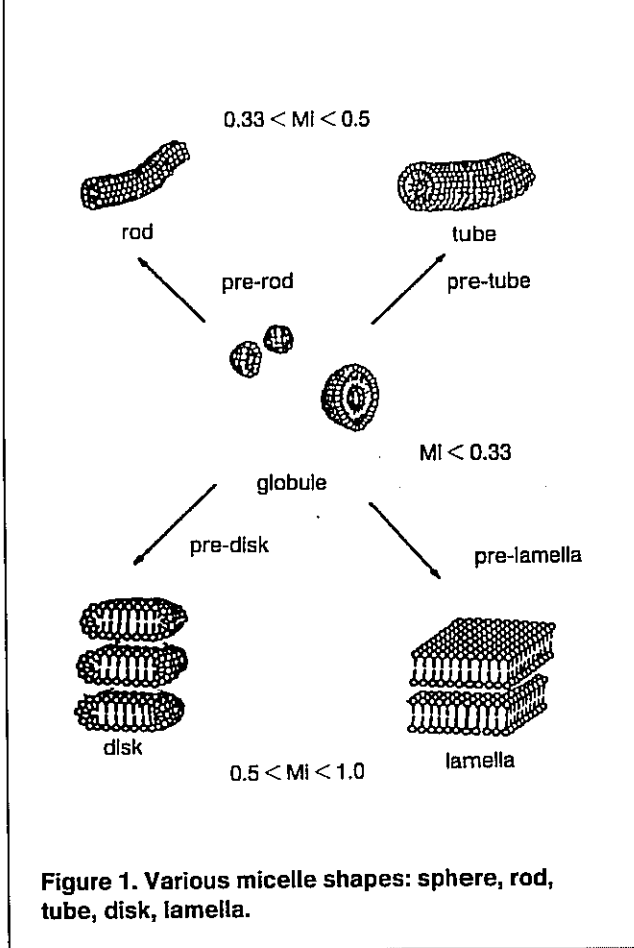

Figure 1. Various micelle shapes: sphere, rod, tube, disk, lamella.

This LC phase forms a kind of protective skin around the emulsion droplets, more effectively protecting them against coalescence. The viscous-elastic nature of the skin further contributes to coalescence resistance. Modification of the attracting forces between emulsion droplets by the presence of liquid crystals decreases the rate of coagulation and therefore suppresses creaming.

The formation of a gel network and the accompanying increase in viscosity further adds to the stability, especially in w/o emulsions. It is therefore of interest to design the derivative molecule in such a way that the formation of these favorable surfactant association structures are stimulated.

An important property of surface active materials is that, in strongly polar solvents above a certain concentration (critical micelle concentration, CMC), aggregates (micelles) are formed. Figure 1 illustrates the different micelle shapes. Using thermodynamics and geometrical considerations, Israelachvili, Ninham, and Mitchell[29-31] devised a model and a formula to describe the dominant micelle shape. Model and formula are both base on surfactant chain length, hydrocarbon chain volume, and cross-sectional area of the polar head group of a surfactant molecule.

Table II. PG-3 Beeswax.	
Physical form	Amorphous wax
Color	White to light yellow
Odor	Neutral to wax-like
Acid value	< 0.8 mg KOH/g wax
Saponification value	80-94 mg KOH/g wax
Peroxide value	< 3mEq/g wax
Melting point range	63 to 73°C
Flash point	> 250°C.
Density @25°C	0.93 to 0.97
Solubility	Similar to beeswax
Toxicology and dermatological properties (Methode Journal Officiel Français)	Skin Irritation = 0.3 (non-irritating) Eye Irritation = 7.0 (very slightly irritating) Classification = nontoxic group
Stabilization	No stabilizers or antioxidants added (naturally present)

$$Mi = v/l_c\, a_o$$

where v = the volume of the hydrocarbon chain
(first estimate $v = (27.4 + 26.9n)$ Å³)

n = a value somewhat smaller than the number of C-atoms in the hydrocarbon tail)

l_c = the critical (fully extended) length of the surfactant chain (ca. 80-90%)
(first estimate $l_c = (1.5 + 1.26n)$ Å)

a_o = the optimal cross-sectional area per polar head group of the surfactant at a planar interface (for symbols see ref. 18, 19)

$$a_o = \sqrt{(2\pi e^2\ D/\varepsilon\,\delta)}\ \text{Å}^2$$

$Mi < 0.33$ = spherical micelles
$0.33 < Mi < 0.5$ = cylindrical micelles
$0.5 > Mi > 1.0$ = lamellar (bilayer) structures or vesicles
$Mi > 1.0$ = inverse structures

In this equation, Mi denotes the dimensionless micelle number. Israelachvili et al. aptly called it the packing ratio; Becher[32] called this parameter the MN number. Thus a quantitative indication is given, predicting which amphiphilic molecules or combinations of amphiphilic molecules give rise to lamellar liquid crystal formation. Of course, actual liquid crystal formation also depends on a combination of other variables, such as temperature, ingredient concentrations, the presence of other surface active agents, and the type of oil phase.

This model explains many of the influences, mostly in terms of the effective volume parameter, v, and the area, a_0. The equation expresses a relationship for both a given quantity of a surfactant molecule alone and also of the system as a whole. Exceptions exist, but as situations become more complex, the packing

Table III. Ingredients for o/w emulsions with and without PG-3 Beeswax		
	Emulsion A (without)	Emulsion B (with)
A) Ceteareth-25	3.0	3.0
Ceteareth-6	2.0	2.0
Cetyl alcohol	5.5	5.5
PG-3 Beeswax	—	1.0
Propylene glycol dioctanoate	11.0	10.0
Dimethicone 200 cS	0.2	0.2
B) Preservative mixture	1.0	1.0
Water	67.0	67.0
Carbomer 940 (2% sol.)	5.0	5.0
C) Tris (hydroxymethyl) aminomethane (THAM)	0.2	0.2
Water	4.8	4.8
D) Fragrance	0.3	0.3
	100.0%	100.0%

The general picture which emerges from this approach is that two-tailed surfactant molecules are favored over single tailed (for example lecithin in microemulsions and liposomes), a long hydrocarbon tail over a short hydrocarbon tail, and a short chain hydrophilic head over a long chain hydrophilic head. In short, surfactants with relatively low HLB- values are favored for micelle formation. This relation represents a way to formulate by use of the well known HLB-concept.[29-33]

Use as Emulsion Stabilizer and Consistency Regulator

In emulsions, PG-3 beeswax contributes to spreadability and lends a smooth, satin-like feeling to the skin.

Starting from an existing formulation, it is possible to replace a part of the components from the oil or wax phase by PG-3 beeswax. This acts as a modifier, contributing to stability and improving the rheological behavior of the modified formulation. Addition of only 1% PG-3 beeswax, replacing some of the propylene glycol dioctanoate, (Table III) results in a surprisingly large change in rheology (Figure 2).

When developing a new product, the advantages of PG-3 beeswax can be used to achieve specific rheological effects. It should be applied in concentrations amounting to at least 10-15% of the oil phase (see Table IV).
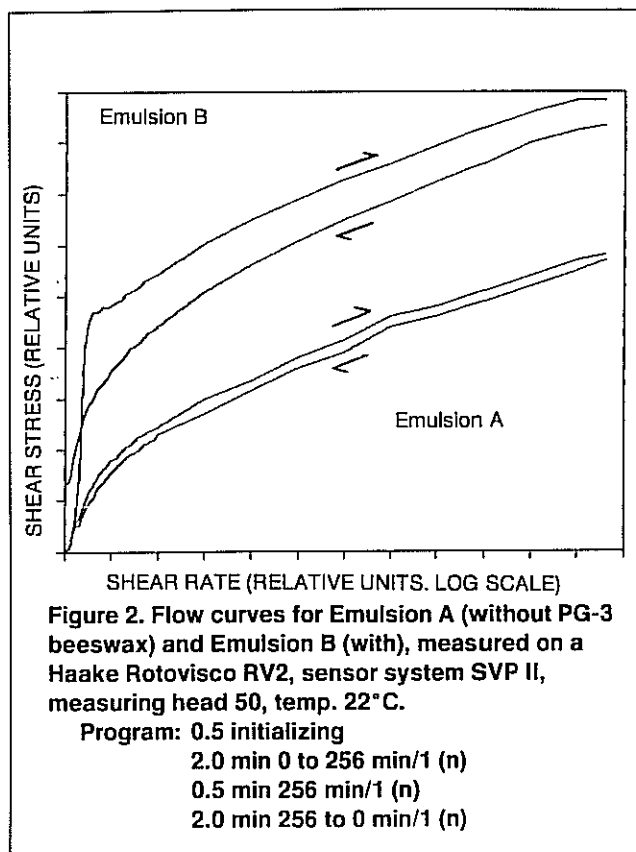
PG-3 beeswax is not intended to replace beeswax

Figure 2. Flow curves for Emulsion A (without PG-3 beeswax) and Emulsion B (with), measured on a Haake Rotovisco RV2, sensor system SVP II, measuring head 50, temp. 22°C.
Program: 0.5 initializing
2.0 min 0 to 256 min/1 (n)
0.5 min 256 min/1 (n)
2.0 min 256 to 0 min/1 (n)

tion) which are partly lost when this derivative is combined with the saturated fatty acids in beeswax (tetracosanoic, hexacosanoic, etc.). The same problem exists with commercially available saturated fatty acids (palmitic, stearic, etc.). It is compatible with unsaturated fatty acids and isostearic acid.

A New Oil-Gelling Agent

PG-3 beeswax will give stable, thixotropic, nongranular gels in a large variety of cosmetic oils and oil mixtures without the incorporation of inorganic rheological additives. These nontransparent gels are easy to produce. They can be vehicles for such materials as sunscreen agents, oil-soluble vitamins, and oil-soluble plant extracts.

Table V shows concentrations of PG-3 beeswax needed to gel specific oils. The amount required to produce a thixotropic gel is dependent on the oil used. Viscosity and polarity of the oil play important roles. Best results are obtained if cooling is slow, especially for the less viscous oils. In the silicone oil group, gelification was mainly achieved for the less polar phenyl methicones.

This beeswax derivative will also gel oil mixtures. For example, a mixture of equal quantities of isopropyl myristate, oleyl oleate C_8-C_{12}-triglyceride, paraffin oil, jojoba oil and avocado oil with 13% PG-3 beeswax produced a smooth, stable gel with excellent skin-feel. A mixture of natural oils (equal amounts of avocado, jojoba, sesame and sweet almond oils) with 9% PG-3 beeswax also provides excellent gellification.

Both of the above gels survived many temperature cycles (20-50°C.) without showing any decrease in quality. The liquid crystal formation, interlinked by a temperature reversible and a largely mechanically reversible network formation, is responsible for the increased stability of the oil phase and for the gels produced. This contributes to the improved stability of emulsions, especially of the oil-continuous w/o type.

PG-3 beeswax is a promising ingredient for decorative cosmetics because it can stabilize pigment suspensions and assist in the dispersion step itself. Pigment dispersion is accomplished when aggregates are broken apart into their primary particles, in a dissimilar medium. The free fatty acids of our beeswax derivative assist wetting by removing gases or moisture from pigment crystal surfaces, to be replaced by medium. With mechanical means of mixing, deagglomeration is accomplished.

To reduce reaggregation and increase stability, the Van Der Waals forces between primary pigment particles must be reduced. Through charge stabilization (electrical repulsion) and steric stabilization (steric hindrances) by the PG-3 beeswax, pigment particles are prevented from coming back together.

The polar groups of the beeswax derivative assist in the deagglomeration of powder aggregates by the formation of a liquid crystalline phase, which contributes to increased stability. The liquid crystal's protective skin around suspended particles and the gel network furnish resistance to particle coagulation and sedimentation.

In the laboratory, a pigment dispersion gel was made. PG-3 beeswax was melted and heated to about 85°C, then (unmilled technical grade) pigment was added. The mixture was stirred and ground with a simple glass rod until visible agglomerates disappeared. Next, the oil or oil mixture was slowly added under stirring and reheating. Cooling to room temperature with moderate stirring gave a homogeneously pigmented gel.

Figure 3 shows the excellent size distribution of the pigment particles and the liquid crystalline character of a dispersion of technical grade pigment (10%

Table IV. Water in oil emulsion		
Oil phase:		
	Sorbitan sesquioleate	3.0
	Glyceryl monostearate	4.0
	Steareth 45	1.0
	PG-3 Beeswax	6.0
	Sweet almond oil	2.0
	Jojoba oil	1.5
	Cetyl alcohol	1.5
	Paraffin oil	14.0
	Isopropyl palmitate	2.0
Water phase:		
	Glycerol	2.0
	Preservative mixture	1.0
	Water	62.0
		100.0%

Table V. Gelling cosmetic oils	
Type of oil:	% PG-3 Beeswax to form gel
Triglycerides:	
Avocado oil	8.0
Castor oil	6.5
Sesame oil	7.8
Sweet almond oil	9.0
Olive oil	9.1
C_8 to C_{12} triglyceride	15.3
Straight chain esters:	
Jojoba oil	12.3
Oleyl oleate	13.0
Branched chain esters:	
Isopropylmyristate (IPM)	25.0
Propylene glycol diesters:	
1,2 Propylene glycol dioctanoate	22.5
Hydrocarbons:	
Paraffin oil	15.2
Branched oil; Isoeicosane and Isooctahexacontane (67%: 33%)	22.9
Silicon oil:	
Phenylmethicones	29.0

Formula 1. Suggested lipstick formulation

PG-3 Beeswax	14.0%
Rice bran wax	3.0
Carnauba wax	2.0
Ozokerite	5.0
Oleyl alcohol	10.0
Propylene glycol dioctanoate	4.0
Acetylated lanolin	1.0
Jojoba oil	5.0
Castor oil	43.7
BHT	0.1
TiO_2 (rutile)	3.5
Eosine (red pigments)	0.5
Organic pigments	7.2
Fragrance	1.0

Formula 2. Lipstick

PG-3 Beeswax	16.0%
Castor oil	41.0
Paraffin oil	25.0
Synthetic candelilla	5.0
Isopropyl myristate	4.0
Lanolin	2.0
Ozokerite	2.0
Carnauba #1 Yellow	1.0
D & C Red #7	4.0

Formula 3. Blue black mascara

Phase A	
PG-3 Beeswax	10.0%
Synthetic candelilla	7.0
Oleic acid	6.0
Glyceryl monostearate	3.0
Phase B	
Water	65.0
TEA	1.0
Propylene glycol	1.0
Phase C	
Iron oxide	3.5
7010 Cosmetic Navy	
Blue (Whittaker Clark)	2.5
Titanium dioxide	1.0

Formula 4. Cream stick antiperspirant (forms clear film)

PG-3 Beeswax	10.0%
Cetearyl alcohol	10.0
Glyceryl monostearate	9.0
Propylene glycol stearate	7.0
PEG-20	6.5
Propylene glycol dioctanoate	15.0
Isostearic acid	10.0
Propylene glycol	5.0
Cyclomethicone	5.0
Isopropyl myristate	2.0
Aluminum chlorohydrate	20.0
Titanium dioxide	0.5

80% avocado oil (prepared as mentioned above). The smooth, nongranular effect is immediately noticed when the resulting gel is applied to the skin.

When castor oil is used in the formulation, very firm gels result, especially with inorganic pigments. The amount of PG-3 beeswax needed to achieve good dispersion depends on the type of pigment. Inorganic pigments require a greater concentration (by weight) than organic pigments.

These properties, and its low volume contraction upon cooling, make PG-3 beeswax very suitable for lipstick (and other stick) formulations . An example of a lipstick formulation is shown in Formula 1. Formulas 2-4 give examples of its use in cosmetics which sometimes pose formulating difficulties due to incompatibility of the components.

The lipstick in Formula 2 utilizes PG-3 beeswax as a gelling agent with the ability to deagglomerate unmilled pigment particles. This lipstick has a high concentration of oils, producing a product which has high gloss and color development, is long wearing, waterproof, and which allows for even and smooth application, giving a soft silky texture and moisture barrier.

The mascara, Formula 3, is easily prepared. Phase A is added to phase B at 80°C under agitation. When the temperature falls to 45 to 50°C, phase C (premixed unmilled pigment) is added under continuous mixing. This product is fast drying, long lasting, easy to apply and very stable.

The final example, Formula 4, is a cream stick antiperspirant and takes advantage of the dispersion ability of PG-3 beeswax. We have used components which are not soluble, and have formed a very stable,
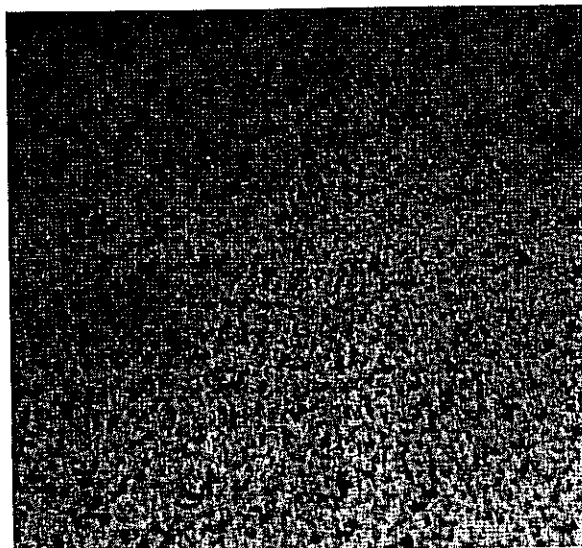

Figure 3. Photomicrograph of pigment dispersion using PG-3 beeswax.

like feel. It rubs into the skin, forming a clear film.

Conclusion

This study has shown that a derivative of natural beeswax, PG-3 beeswax, can improve the quality of various cosmetics. Improvements were seen in emulsion stability, oil gelling ability, and pigment dispersion properties. Individual advantages can be utilized by simply substituting this new material into existing formulas, but optimal expression of all its cosmetic-enhancing attributes is best seen when entirely new products are formulated.

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Address correspondence to Steven L. Puleo, Vice President R&D, Koster Keunen, Inc., 90 Bourne Boulevard, Sayville NY 11782 USA.

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